

Low-Temperature Air-Sinterable Lanthanum Calcium Chromite with Chromium Deficit for SOFC Separator

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The low temperature sintering characteristic of lanthanum calcium chromites has been investigated. A chromium deficient lanthanum calcium chromite, $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$, which was prepared by precipitation from nitrate solution using oxalic acid, was found to be sintered easily at low temperatures in air. A relative density of 94% was obtained after heating at 1473 K for 100 h, at 1573 K for 5 h or at 1673 K without holding time. The chromium deficient lanthanum calcium chromite may be used for planar SOFC separators, being applicable to a co-firing fabrication of planar SOFCs.

1 INTRODUCTION

A cell component called interconnector or separator is indispensable for stacking planar solid oxide fuel cells (SOFCs). This material should play twofold roles, that is, separating fuel gas from air, and electrically interconnecting single cells. As an oxide separator, lanthanum chromite is the most promising, since this perovskite-type oxide is chemically quite stable both in air and hydrogen and high electrical conductivities can be obtained by alkaline earth doping. However, lanthanum chromite has been widely recognized as a poorly sinterable material. Since the separator of planar SOFCs should be gaseously tight, it is crucial to find an appropriate way of fabricating dense plates of the lanthanum chromites. Several attempts¹⁻⁷⁾ have been made to densify lanthanum chromites; for example, Flandermeier et al.¹⁾ found that sintering aids such as fluoride mixtures are effective in pre-

paring separator dense plates for monolithic cells. Anderson and co-workers^{2,3)} have investigated effects of doping other transition metals (Co etc.) in B-sites of perovskite structure. Quite recently, Sakai et al.⁴⁾ have found that a slight chromium deficiency enhances the sinterability of lanthanum calcium chromite, $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ ($0 < x < 0.4$, $y < 0.05$) and more than 94% of the theoretical density is obtained at 1873 K for 5–10 h in air without sintering aids.

We have investigated sintering properties of chromium doped lanthanum strontium manganites to find an appropriate way of preventing air electrodes from being degraded due to morphological change during sintering⁸⁾. During investigation on lanthanum chromites as one end member of the lanthanum chromite-manganite system, we realized that lanthanum chromites exhibit some symptom of starting sintering at a temperature as low as 1273 K. Since the low temperature sintering is quite important in tape cast technique of fabricating planar SOFCs, we have investigated sintering characteristics of these powders, although they were adopted originally for (La, Sr)(Mn, Cr) O_3 air electrodes. Experimental results have confirmed that the present powders were actually sintered in

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a relatively low temperature region. In this paper, we report the experimental results.

2 EXPERIMENTAL

2.1 Sample powder preparation

Sample powders were prepared as follows: nitrate solutions of La, Ca and Cr were prepared and analyzed by chemical titration method. Three solutions were mixed in selected compositions. In the present study, two compositions were selected; that is, La/Ca/Cr = 70/30/100 (stoichiometric) and 70/32/100, namely, 69/31/98 (Cr deficient). These nitrate solutions were mixed with an excess amount of ethanol solution of oxalic acid which is required to form oxalates of La, Ca, and Cr. Almost all of La^{3+} and Ca^{2+} ions were precipitated as oxalates $\text{La}_2(\text{C}_2\text{O}_4)_3$ or CaC_2O_4 ; however, some part of Cr^{3+} ions remained as $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$. The solutions including precipitates were dried up by blowing air at room temperature. The dried powders were calcined at 633 K for 5 h to be dehydrated; decomposition of the nitrate occurred during this process. Their ethanol suspensions were milled for 12 h in alumina mill with partial stabilized zirconia balls. The samples were dried up and heated in air at a rate of 50 K/h to 1273 K and held at this temperature for 20 h. The milling and heating procedures were repeated twice.

2.2 Sintering behavior

These sample powders were ground in an agate mortar and pressed into pellets (20 mm in diameter and about 1–2 mm thick) under 120 MPa using a small amount of polyvinyl butyral as binder. Pellets were fired at 1373, 1473, 1573 and 1673 K; the heating rate was fixed at 100 K/h in every run and the holding time at the selected temperatures was changed from 0 to 232 h. Zero hour means no holding time at the fired temperature in this paper. Density of fired pellets was determined from observed values of size and weight or directly by Archimedes method. Relative density was derived using the theoretical value determined from the experimental lattice parameters and unit formula.

3 RESULTS AND DISCUSSION

3.1 Characteristics of sample powders

The sample powders were analyzed by X-ray diffraction technique. These lanthanum chromites were the orthorhombic perovskites; the lattice parameters obtained were $a=0.5450$ nm, $b=0.5443$ nm and $c=0.7675$ nm for the stoichiometric composition and $a=0.5452$ nm, $b=0.5436$ nm and $c=0.7689$ nm for the Cr deficient composition, respectively. The X-ray diffraction (XRD) pattern showed that no compound other than the perovskite phase was found in the stoichiometric samples, whereas the chromium deficient samples contained a very small amount of CaCrO_4 in addition to the perovskite phase. Although the initial atomic ratio of chromium to combined lanthanum and calcium, $N(\text{Cr})/\{N(\text{Ca}) + N(\text{La})\}$, was fixed at 1.02 in the chromium deficient samples, observed phases were CaCrO_4 and the perovskite phase both of which have the atomic ratio of 1. This implies the following two possibilities; that is, (1) the perovskite phase may be chromium deficient (Ca substitution, vacancy formation or stacking fault between (La, Ca)O and CrO_2 layers), or (2) there may be a third phase having the atomic ratio less than 1, which was not detected in XRD results. Although La_2CrO_6 phase was frequently observed in samples prepared by Sakai et al.⁴⁾, the present chromium deficient samples did not contain La_2CrO_6 . This compound decomposes to form oxochromates, $\text{La}_7\text{Cr}_2\text{O}_{16}$ and $\text{La}_{16}\text{Cr}_7\text{O}_{44}$, as intermediate products⁹⁾. Furthermore, $\text{Ca}_3\text{Cr}_2\text{O}_8$ and related compounds are known in the CaO rich region in the Ca–Cr–O system. By taking account into these phases appearing near 1273 K, it is most likely that the present chromium deficient samples contain such compounds as a third phase.

The particle size of the Cr deficient lanthanum calcium chromite powders was about 1 μm in diameter on average as shown in Fig. 2(a). This SEM photograph shows that particles were partly aggregated. This is due to a relatively long holding time at 1273 K. In other words, the sintering of Cr deficient lanthanum chromite

may already start at 1273 K. On the other hand, grains of the stoichiometric sample are small and agglomeration was not observed (Fig. 2(b)).

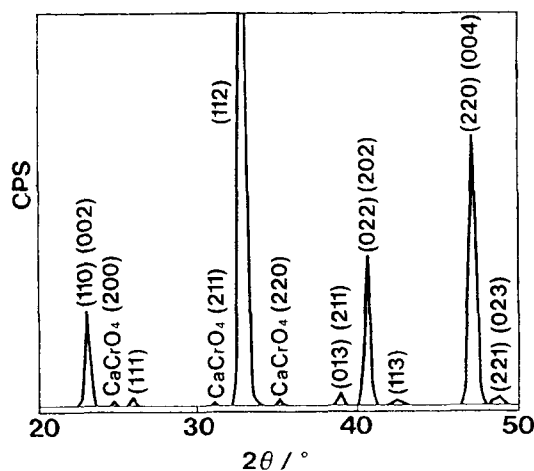


Fig. 1 X-ray diffraction pattern of $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$ which fired twice at 1273 K for 20 h in air.

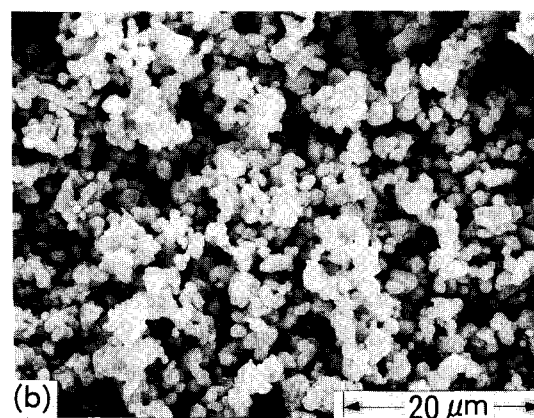
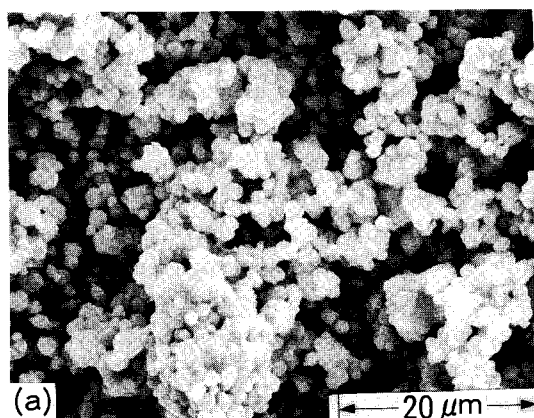


Fig. 2 SEM photographs of $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$ (a) and $\text{La}_{0.70}\text{Ca}_{0.30}\text{CrO}_3$ (b) fired twice at 1273 K for 20 h in air.

3.2 Sintering behavior

Figures 3, 4(a) and 4(b) show the relative density as a function of holding time with a parameter of firing temperature. The stoichiometric lanthanum calcium chromites showed a poor sinterability. The relative density of the stoichiometric lanthanum calcium chromite was about 60%, although its slight dependence can be seen on sintering temperature and holding time.

It should be noted that sintering of the Cr deficient lanthanum calcium chromite depends on heating temperature and holding time. The marked region in Figs. 4(a) and 4(b) is of relative densities more than 94%; sintered ceramics in this region can provide gaseous tightness which is required for SOFC separators. Figure 4(a) shows that even at 1373 K, densification to 90% of theoretical density was observed for 50 h. It attained 94% at 1473 K for 100 h. Especially, in the case of firing at 1573 K and 1673 K, this was densified to 94% for 5 h and no holding time, respectively.

In order to make clear the effect of temperature on sintering, the relative density of Cr deficient lanthanum chromite is plotted as a function of temperature in Fig. 4(b). Each data point in this figure corresponds to that at the holding time = 0 h in Fig. 4(a). Figure 4(b) can be regarded as the shrinkage characteristics on continuous heating at the rate of 100 K/h. The main shrinkage took place in the temperature region of 1373 to 1673 K. This is one of the lowest

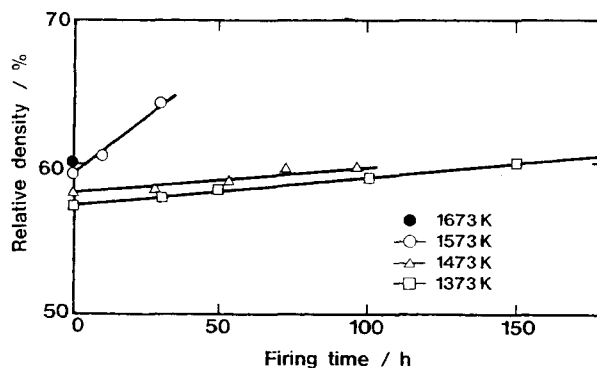


Figure 3

Fig. 3 The relative density of $\text{La}_{0.70}\text{Ca}_{0.30}\text{CrO}_3$, as a function of holding time with a parameter of firing temperature.

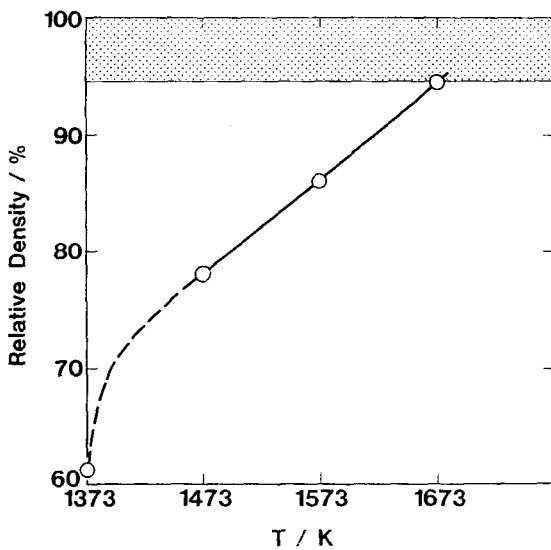
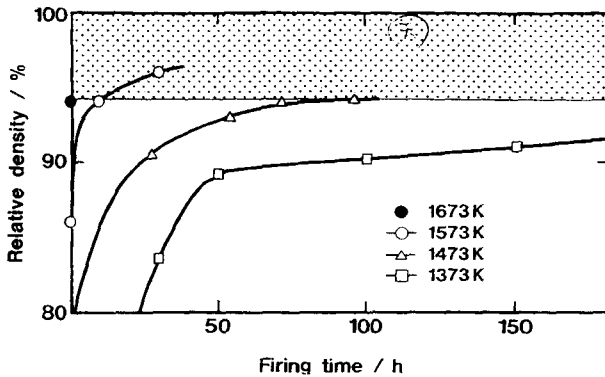


Fig. 4 (a) The relative density of $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$, as a function of holding time with a parameter of firing temperature.
(b) The relative density of $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$, as a function of temperature.

in the reported sintering temperature of lanthanum chromites.

Figures 5(a) and 5(b) show SEM images of surface and cross section of the present samples. The grain growth took place uniformly and pores were very small. The shrinkage ratio of vertical to horizontal directions is usually equal to unity; for example, it was observed to be about 1.0 for 8 mole % yttria doped zirconia (TOSO; TZ-8Y) pellet. However, the Cr deficient lanthanum

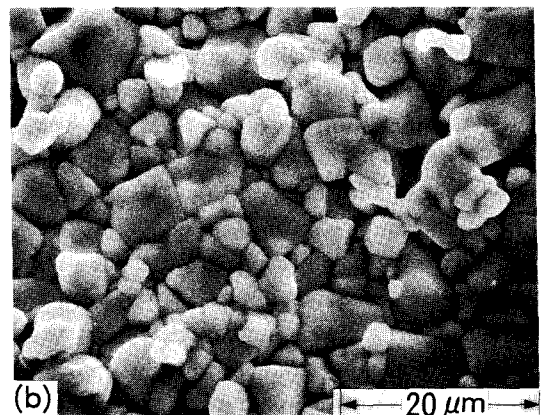
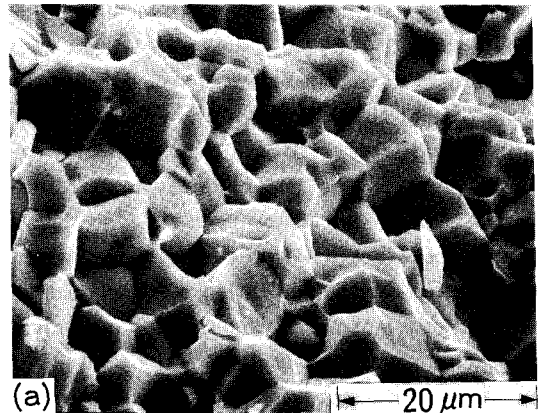


Fig. 5 SEM photographs of cross section (a) and surface section (b) of $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$ fired at 1573 K for 5 h in air.

calcium chromite was about 0.93. Reexamination of the results by Sakai et al.⁴ revealed that a similar phenomenon occurred in their sintering experiments at 1873 K.

3.3 Sintering mechanism

The present results revealed that even at low temperatures, the sinterability of lanthanum calcium chromites strongly depends on the chromium content. This suggests the strong correlation between sinterability and thermodynamic activity of chromium. Yokokawa et al.¹⁰ have recently reasoned, from the results of thermodynamic analysis on phase relations and equilibrium vapor pressures, that poor sinterability at 1873 K may be due to the formation of Cr_2O_3 as a result of incongruent vaporization—

heterogenization of LaCrO_3 . At lower temperatures (1273–1673 K), however, the vapor pressures of chromium oxides are considered to be lower than at 1873 K. As shown in Figs. 2(a) and 2(b), the difference in sintering between the stoichiometric and the chromium deficient samples can be seen clearly even at 1273 K. This implies that other processes than the incongruent vaporization–heterogenization mechanism may take place to make sintering strongly dependent on the chromium content.

To obtain further information about sintering behavior of the present samples, additional experiments were made using the same powders of the chromium deficient samples two month after the first series of experiments given in Figs. 3 and 4. Figure 6(a) shows the SEM images of a sample sintered at 1573 K for 5 h, which should be compared with Fig. 5(b). The following differences can be seen in these photographs; the first sample in Fig. 5(b) consists of various sizes of grains, whereas the sample in Fig. 6(a) consists mainly of large grains, and furthermore, their grain boundaries became obscure; this is probably due to a thin layer of non-crystalline substances. The more striking feature shown in Fig. 6(b) was obtained in a sample sintered at 1473 K without holding time. The aggregation of powders suggests that a liquid phase was formed during heating. Since the first series of experiments at 1473 K given in Fig. 4(a) showed no anomalous behavior, it is most likely that sintering characteristics of the powders were changed after the first series of experiments. As described in 3.1 section, the present samples contained a small amount of CaCrO_4 ; this compound is known to decompose into $\text{Ca}_3\text{Cr}_2\text{O}_8$ and CaCr_2O_4 and then to form a liquid phase at about 1300 K and its related CaO rich compound, $\text{Ca}_3\text{Cr}_2\text{O}_8$, melt incongruently around 1500–1600 K¹¹). These available phase relations in the Ca–Cr–O system suggests that the minor phases in the present chromium deficient samples may melt during the sintering process. In addition, CaCrO_4 dissolves easily to water. Therefore, there is some possibility that the present samples reacted with moisture in air

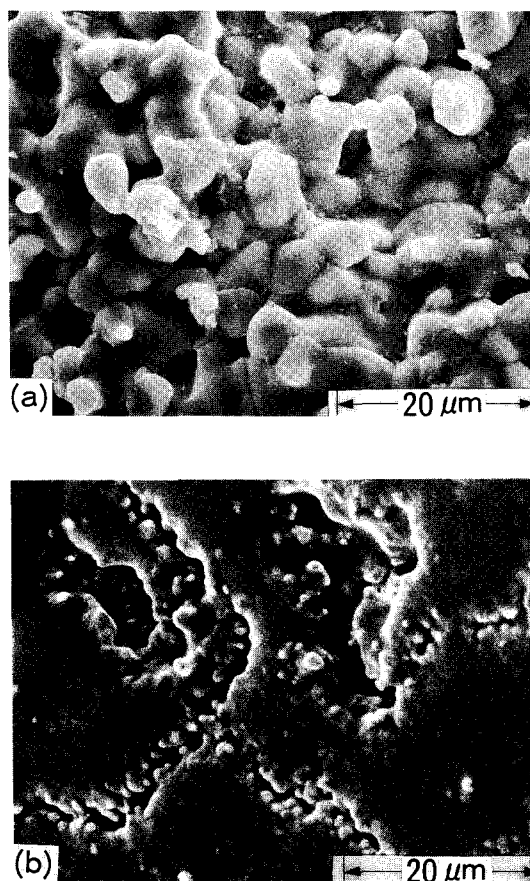


Fig. 6 SEM photographs of surface section of melted $\text{La}_{0.70}\text{Ca}_{0.32}\text{CrO}_3$ particle fired at 1573 K for 5 h (a), 1473 K for 0 h (b).

and as a result, the sintering characteristics of powders were changed.

This suggests that the phase relations of the $\text{CaO} - \text{La}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ system, especially the formations of liquid phase, in the temperature region of 1273–1673 K are quite important to understand the sinterability of lanthanum calcium chromites.

3.4 Application to SOFCs

These low temperature sintering characteristics are important particularly in applying to fabrication of a planar SOFC. As previously reported¹²), lanthanum strontium manganite air electrodes lose their electrode catalytic activity during a long-term high temperature heat treatment, partly because their morphological

structure changes at high temperatures (>1473 K). To co-fire the lanthanum chromite separator together with the lanthanum manganite air electrode, it is therefore desirable to lower the sintering temperature of the lanthanum chromite. In addition to this, use of sintering aids is undesirable because such aids may damage other cell components to be co-fired. In view of these problems associated with the fabrication method of planar SOFC by co-firing, the present low temperature sintering without sintering aids is quite significant.

Since the low temperature sintering characteristics are of technological importance, it is necessary to clarify the sintering mechanism of chromium deficient lanthanum calcium chromites. A further investigation on the effects of sample preparation method and phase relations on sintering characteristics of lanthanum calcium chromites is in progress.

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